



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : <b>A61K 7/48</b></p>	<b>A1</b>	<p>(11) International Publication Number: <b>WO 98/22085</b></p> <p>(43) International Publication Date: 28 May 1998 (28.05.98)</p>		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;"> <p>(21) International Application Number: <b>PCT/US97/20566</b></p> <p>(22) International Filing Date: 13 November 1997 (13.11.97)</p> <p>(30) Priority Data:  <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div>9624305.0      22 November 1996 (22.11.96)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9710697.5      23 May 1997 (23.05.97)</div> <div>GB</div> </div> </p> <p>(71) Applicant (for all designated States except US): THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): BELL, Michael, David [GB/GB]; 2 South Road, Englefield Green, Egham, Surrey TW20 0RL (GB). NAWAZ, Zahid [GB/GB]; 6A Aston Road, Ealing, London W5 2RL (GB). CSELIK, Frank [GB/GB]; 20 Green Hill Gate, High Wycombe, Bucks HP13 5QQ (GB).</p> <p>(74) Agents: REED, T., David et al.; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p> </td> <td style="width: 50%; vertical-align: top; border: none;"> <p>(81) Designated States: AU, CA, CN, CZ, HU, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b>  <i>With international search report.</i></p> </td> </tr> </table>			<p>(21) International Application Number: <b>PCT/US97/20566</b></p> <p>(22) International Filing Date: 13 November 1997 (13.11.97)</p> <p>(30) Priority Data:  <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div>9624305.0      22 November 1996 (22.11.96)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9710697.5      23 May 1997 (23.05.97)</div> <div>GB</div> </div> </p> <p>(71) Applicant (for all designated States except US): THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): BELL, Michael, David [GB/GB]; 2 South Road, Englefield Green, Egham, Surrey TW20 0RL (GB). NAWAZ, Zahid [GB/GB]; 6A Aston Road, Ealing, London W5 2RL (GB). CSELIK, Frank [GB/GB]; 20 Green Hill Gate, High Wycombe, Bucks HP13 5QQ (GB).</p> <p>(74) Agents: REED, T., David et al.; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>	<p>(81) Designated States: AU, CA, CN, CZ, HU, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b>  <i>With international search report.</i></p>
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<p>(54) Title: COSMETIC COMPOSITIONS</p> <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 20px;"> <div style="text-align: center;"> <math display="block">\begin{array}{c} R^2 \\   \\ R^1 - C - (CH_2)_x - C \begin{array}{l} \nearrow O \\ \searrow OR^4 \end{array} \\   \\ R^3 \end{array} \quad (I)</math> </div> <div style="text-align: center;"> <math display="block">R^5 - \overset{\overset{O}{\parallel}}{C} - OR^6 \quad (II)</math> </div> </div> <p>(57) Abstract</p> <p>A cosmetic composition suitable for topical application to the skin or hair comprising: (a) a liquid, polyol carboxylic acid ester having a polyol moiety and at least 4 carboxylic acid moieties, wherein the polyol moiety is selected from sugars and sugar alcohols containing from about 4 to about 8 hydroxyl groups, and wherein each carboxylic acid moiety has from about 8 to about 22 carbon atoms, and wherein said liquid polyol carboxylic acid ester has a complete melting point of less than about 30 °C; (b) an emollient material selected from compounds having formula (I), wherein R<sup>1</sup> is selected from H or CH<sub>3</sub>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently selected from C<sub>1</sub>-C<sub>20</sub> straight chain or branched chain alkyl, and x is an integer of from 1-20, and compounds having formula (II), wherein R<sup>5</sup> is selected from optionally hydroxy or C<sub>1</sub>-C<sub>4</sub> alkyl substituted benzyl and R<sub>6</sub> is selected from C<sub>1</sub>-C<sub>20</sub> branched or straight chain alkyl; and mixtures thereof. The compositions herein provide improved skin feel, skin smoothness, skin softness and skin care benefits.</p>				

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## COSMETIC COMPOSITIONS

### Technical Field

The present invention relates to cosmetic compositions. In particular it relates to cosmetic compositions which provide improved moisturization, skin feel, skin softness, skin smoothness benefits, together with excellent rub-in and absorption characteristics. The compositions also display excellent stability characteristics at normal and elevated temperatures.

### Background of the Invention

Skin is made up of several layers of cells which coat and protect the keratin and collagen fibrous proteins that form the skeleton of its structure. The outermost of these layers, referred to as the stratum corneum, is known to be composed of 25nm protein bundles surrounded by 8nm thick layers. Anionic surfactants and organic solvents typically penetrate the stratum corneum membrane and, by delipidization (i.e. removal of the lipids from the stratum corneum), destroy its integrity. This destruction of the skin surface topography leads to a rough feel and may eventually permit the surfactant or solvent to interact with the keratin, creating irritation.

It is now recognised that maintaining the proper water gradient across the stratum corneum is important to its functionality. Most of this water, which is sometimes considered to be the stratum corneum's plasticizer, comes from inside the body. If the humidity is too low, such as in a cold climate, insufficient water remains in the outer layers of the stratum corneum to properly plasticize the tissue, and the skin begins to scale and becomes itchy. Skin permeability is also decreased somewhat when there is inadequate water across the stratum corneum. On the other hand, too much water on the outside of the skin causes the stratum corneum to ultimately sorb three to five times its own weight of bound water. This swells and puckers the skin and results in approximately a two to three fold increase in the permeability of the skin to water and other polar molecules.

Thus, a need exists for compositions which will assist the stratum corneum in maintaining its barrier and water-retention functions at optimum performance in spite of deleterious interactions which the skin may encounter in washing, work, and recreation.

Conventional cosmetic cream and lotion compositions as described, for example, in Sagarin, *Cosmetics Science and Technology*, 2nd Edition, Vol.1, Wiley Interscience (1972) and *Encyclopaedia of Chemical Technology*, Third Edition, Volume 7 are known to provide varying degrees of emolliency, barrier and water-retention (moisturizing) benefits. However, they can also suffer negatives in terms of skin feel (i.e. not providing the desired skin softness or skin smoothness benefits) and have poor rub-in and slow absorption into the skin.

Thus, there remains a need for compositions which will assist the stratum corneum in maintaining its water gradient, but which do so with improved skin feel, skin softness and skin smoothness and improved absorption into the skin.

Polyol fatty acid polyester compounds are known for use in skin care compositions. For example, EP-A-458600, EP-A-466410, EP-A-519727 and EP-A-587288 disclose compositions containing polyol fatty acid polyester compounds for use in skin care compositions.

In addition, compounds such as isopropyl isostearate, glycerol monostearate and isopropyl myristate are known for use in skin care compositions for providing emollient properties.

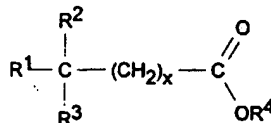
It has now been surprisingly found that by incorporating a particular polyol fatty acid polyester material into a cosmetic emulsion composition together with a particular emollient compound, a composition is provided which provides enhanced skin feel, skin softness and skin smoothness benefits. The compositions herein also providing excellent moisturisation, rub-in and absorption characteristics.

#### Summary of the Invention

According to one aspect of the present invention there is provided a cosmetic composition suitable for topical application to the skin or hair comprising:

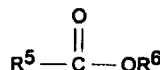
- (a) liquid, polyol carboxylic acid ester having a polyol moiety and at least 4 carboxylic acid moieties, wherein the polyol moiety is selected from sugars and sugar alcohols containing from about 4 to about 8 hydroxyl groups, and wherein each carboxylic acid moiety has from about 8 to about 22 carbon atoms, and wherein said liquid polyol carboxylic acid ester has a complete melting point of less than about 30°C;

- (b) an emollient material selected from compounds having the formula (I):



wherein  $\text{R}^1$  is selected from H or  $\text{CH}_3$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently selected from  $\text{C}_1$ - $\text{C}_{20}$  straight chain or branched chain alkyl, and  $x$  is an integer of from 1-20,

and compounds having the formula (II):



wherein  $\text{R}^5$  is selected from optionally hydroxy or  $\text{C}_1$ - $\text{C}_4$  alkyl substituted benzyl and  $\text{R}^6$  is selected from  $\text{C}_1$ - $\text{C}_{20}$  branched or straight chain alkyl; and mixtures thereof.

The compositions of the invention provide improved skin feel, skin softness and skin smoothness benefits and/or improved rub-in/absorption characteristics.

According to a further aspect of the present invention there is provided a cosmetic method of treatment of the skin comprising applying to the skin a composition according to the present invention.

#### Detailed Description of the Invention

The compositions of the present invention comprises a liquid polyol carboxylic acid ester component together with an essential emollient component as well as various optional ingredients as indicated below. All levels and ratios are by weight of total composition, unless otherwise indicated. Chain length and degrees of ethoxylation are also specified on a weight average basis.

The term "skin conditioning agent", as used herein means a material which provides a "skin conditioning benefit". As used herein, the term "skin conditioning benefit" means any cosmetic conditioning benefit to the skin including, but not limited to, moisturization, humectancy (i.e. the ability to retain or hold water or moisture in the

skin), emolliency, visual improvement of the skin surface, soothing of the skin, softening of the skin, improvement in skin feel, and the like.

The term "complete melting point", as used herein means a melting point as measured by the well-known technique of Differential Scanning Calorimetry (DSC). The complete melting point is the temperature at the intersection of the baseline, i.e. the specific heat line, with the line tangent to the trailing edge of the endothermic peak. A scanning temperature of 5°C/minute is generally suitable in the present invention for measuring the complete melting points. However, it should be recognised that more frequent scanning rates may be deemed appropriate by the analytical chemist skilled in the art in specific circumstances. A DSC technique for measuring complete melting points is also described in US Patent No. 5,306,514, to Letton et al., issued, April 26, 1994, incorporated herein by reference.

The term "nonocclusive" as used herein, means that the component as so described does not substantially or block the passage of air and moisture through the skin surface.

#### Liquid polyol carboxylic acid ester

As an essential component the compositions herein comprise a liquid, polyol carboxylic acid ester.

The compositions of the present invention preferably comprise from about 0.01% to about 20%, more preferably from about 0.1% to about 15%, and especially from about 1% to about 10% by weight of the polyol ester. The level of polyol ester by weight of the oil in the composition is preferably from about 1% to about 30%, more preferably from about 5% to about 20%. From the viewpoint of providing improved skin softness and smoothness benefits, the weight ratio of the liquid carboxylic acid polyol ester to the emollient material is preferably in the range of from about 5:1 to about 1:5, more preferably in the range of from 2:1 to about 1:2.

The polyol ester preferred for use herein is a nonocclusive liquid or liquifiable polyol carboxylic acid ester. These polyol esters are derived from a polyol radical or moiety and one or more carboxylic acid radicals or moieties. In other words, these esters contain a moiety derived from a polyol and one or more moieties derived from a carboxylic acid. These carboxylic acid esters can also be derived from a carboxylic acid. These carboxylic acid esters can also be described as liquid polyol fatty acid

esters, because the terms carboxylic acid and fatty acid are often used interchangeably by those skilled in the art.

The preferred liquid polyol polyesters employed in this invention comprise certain polyols, especially sugars or sugar alcohols, esterified with at least four fatty acid groups. Accordingly, the polyol starting material must have at least four esterifiable hydroxyl groups. Examples of preferred polyols are sugars, including monosaccharides and disaccharides, and sugar alcohols. Examples of monosaccharides containing four hydroxyl groups are xylose and arabinose and the sugar alcohol derived from xylose, which has five hydroxyl groups, i.e., xylitol. The monosaccharide, erythrose, is not suitable in the practice of this invention since it only contains three hydroxyl groups, but the sugar alcohol derived from erythrose, i.e., erythritol, contains four hydroxyl groups and accordingly can be used. Suitable five hydroxyl group-containing monosaccharides are galactose, fructose, and sorbose. Sugar alcohols containing six -OH groups derived from the hydrolysis products of sucrose, as well as glucose and sorbose, e.g., sorbitol, are also suitable. Examples of disaccharide polyols which can be used include maltose, lactose, and sucrose, all of which contain eight hydroxyl groups.

Preferred polyols for preparing the polyesters for use in the present invention are selected from the group consisting of erythritol, xylitol, sorbitol, glucose, and sucrose. Sucrose is especially preferred.

The polyol starting material having at least four hydroxyl groups is esterified on at least four of the -OH groups with a fatty acid containing from about 8 to about 22 carbon atoms. Examples of such fatty acids include caprylic, capric, lauric, myristic, myristoleic, palmitic, palmitoleic, stearic, oleic, ricinoleic, linoleic, linolenic, eleostearic, arachidic, arachidonic, behenic, and erucic acid. The fatty acids can be derived from naturally occurring or synthetic fatty acids; they can be saturated or unsaturated, including positional and geometrical isomers. However, in order to provide liquid polyesters preferred for use herein, at least about 50% by weight of the fatty acid incorporated into the polyester molecule should be unsaturated. Oleic and linoleic acids, and mixtures thereof, are especially preferred.

The polyol fatty acid polyesters useful in this invention should contain at least four fatty acid ester groups. It is not necessary that all of the hydroxyl groups of the polyol be esterified with fatty acid, but it is preferable that the polyester contain no

more than two unesterified hydroxyl groups. Most preferably, substantially all of the hydroxyl groups of the polyol are esterified with fatty acid, i.e., the polyol moiety is substantially completely esterified. The fatty acids esterified to the polyol molecule can be the same or mixed, but as noted above, a substantial amount of the unsaturated acid ester groups must be present to provide liquidity.

To illustrate the above points, a sucrose fatty triester would not be suitable for use herein because it does not contain the required four fatty acid ester groups. A sucrose tetra-fatty acid ester would be suitable, but is not preferred because it has more than two unesterified hydroxyl groups. A sucrose hexa-fatty acid ester would be preferred because it has no more than two unesterified hydroxyl groups. Highly preferred compounds in which all the hydroxyl groups are esterified with fatty acids include the liquid sucrose octa-substituted fatty acid esters.

The following are non-limiting examples of specific polyol fatty acid polyesters containing at least four fatty acid ester groups suitable for use in the present invention: glucose tetraoleate, the glucose tetraesters of soybean oil fatty acids (unsaturated), the mannose tetraesters of mixed soybean oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated soybean oil fatty acids, xylitol pentaoleate, sucrose tetraoleate, sucrose pentaoleate, sucrose hexaoleate, sucrose heptaoleate, sucrose octaoleate, and mixtures thereof.

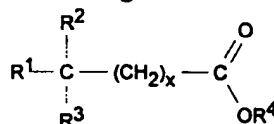
As noted above, highly preferred polyol fatty acid esters are those wherein the fatty acids contain from about 14 to about 18 carbon atoms.

The preferred liquid polyol polyesters preferred for use herein have complete melting points below about 30°C, preferably below about 27.5°C, more preferably below about 25°C. Complete melting points reported herein are measured by Differential Scanning Calorimetry (DSC).

The polyol fatty acid polyesters suitable for use herein can be prepared by a variety of methods well known to those skilled in the art. These methods include: transesterification of the polyol with methyl, ethyl or glycerol fatty acid esters using a variety of catalysts; acylation of the polyol with a fatty acid chloride; acylation of the polyol with a fatty acid anhydride; and acylation of the polyol with a fatty acid,

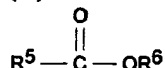
per se. See U.S. Patent No. 2,831,854; U.S. Patent No. 4,005,196, to Jandacek, issued January 25, 1977; U.S. Patent No. 4,005,196, to Jandacek, issued January 25, 1977.

A second essential component of the compositions herein is an emollient material selected from compounds having the formula (I):



wherein R<sup>1</sup> is selected from H or CH<sub>3</sub>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently selected from C<sub>1</sub>-C<sub>20</sub> straight chain or branched chain alkyl, and x is an integer of from 1-20,

and compounds having the formula (II):



wherein R<sup>5</sup> is selected from optionally hydroxy or C<sub>1</sub>-C<sub>4</sub> alkyl substituted benzyl and R<sub>6</sub> is selected from C<sub>1</sub>-C<sub>20</sub> branched or straight chain alkyl; and mixtures thereof.

Preferred for use herein include emollients having the general formula (I) and (II) wherein R<sub>1</sub> is H, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, are independently selected from C<sub>1</sub>-C<sub>4</sub> straight chain alkyl and x is 10 to 18, and wherein R<sub>5</sub> is unsubstituted benzyl and R<sub>6</sub> is C<sub>12</sub>-C<sub>15</sub> alkyl.

Suitable emollients of the types indicated above include but are not limited to methyl isostearate, isopropyl isostearate, C<sub>12</sub>-15 alkyl benzoate, isostearyl neopentanoate.

Particularly preferred for use herein in particularly from the viewpoint of achieving skin softness and smoothness is methyl isostearate, C<sub>12</sub>-15 alkyl benzoate and mixtures thereof.

The emollient material is present in the compositions herein at a level of from about 0.1% to about 10%, preferably from about 0.1% to about 5%, especially from about 1% to about 3% by weight of composition.

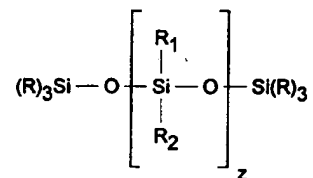
The present compositions can be used for any suitable purpose. In particular, the present compositions are suitable for topical application to the skin or hair. In particular, the skin care compositions can be in the form of creams, lotions, gels, and

the like. Preferably the cosmetic compositions herein are in the form of an oil-in-water emulsion of one or more oil phases in an aqueous continuous phase, each oil phase comprising a single oily component or a mixture of oily components in miscible or homogeneous form but said different oil phases containing different materials or combinations of materials from each other. The overall level of oil phase components in the compositions of the invention is preferably from about 0.1% to about 60%, preferably from about 1% to about 30% and more preferably from about 1% to about 10% by weight.

The present compositions preferably comprise, as either all or a portion of the oil phase or oil phases referred to above a first silicone-containing phase comprising a crosslinked polyorganosiloxane polymer and a silicone oil, wherein the composition comprises 0.1% to about 20%, preferably from about 0.5% to about 10%, more preferably from about 0.5% to about 5%, by weight of composition, of the combination of crosslinked silicone and silicone oil.

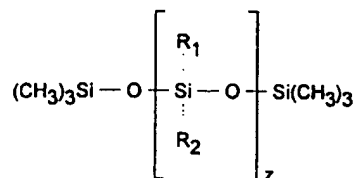
The first silicone-containing phase comprises from about 10% to about 40%, more preferably from about 20% to about 30%, by weight of the first silicone-containing phase, of the crosslinked polyorganosiloxane polymer and from about 60% to about 90%, preferably from about 70% to about 80%, by weight of the first silicone-containing phase, of the silicone oil.

The crosslinked polyorganosiloxane polymer comprises polyorganosiloxane polymer crosslinked by a crosslinking agent. Crosslinking agents for use herein include any crosslinking agents useful for the preparation of crosslinked silicones. Suitable crosslinking agents herein include those represented by the following general formula:



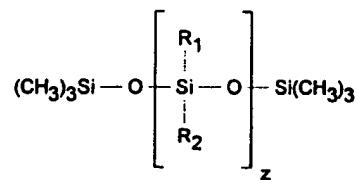
wherein  $R_1$  is methyl, ethyl, propyl or phenyl,  $R_2$  is H or  $-(CH_2)_nCH=CH_2$ , where  $n$  is in the range of from about 1 to about 50,  $z$  is in the range of from about 1 to about 1000, preferably from about 1 to about 100 and  $R$  is an alkyl group having from 1 to 50 carbon atoms.

Preferably the crosslinking agent has the general formula



where  $\text{R}_1$ ,  $\text{R}_2$  and  $z$  are as defined above.

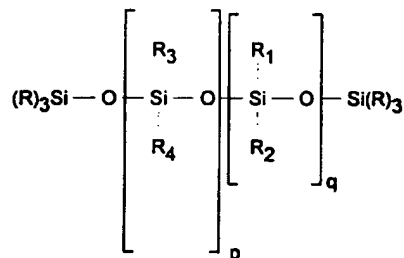
In especially preferred embodiments, the crosslinking agent has the following general formula:



wherein  $z$  is in the range of from about 1 to about 1000, preferably from about 1 to about 100.

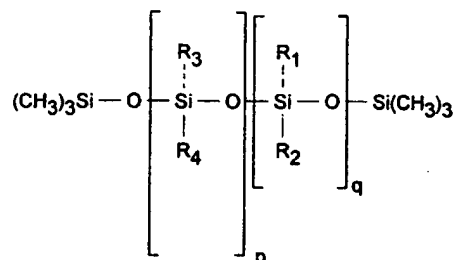
The crosslinked polysiloxane polymer preferably comprises from about 10% to about 50%, more preferably from about 20% to about 30%, by weight the crosslinked polysiloxane polymer, of crosslinking agent.

Any polyorganosiloxane polymers suitable for use in skin care compositions can be used herein. Suitable polyorganosiloxane polymers for use herein include those represented by the following general formula:



wherein  $\text{R}_1$  is methyl, ethyl, propyl or phenyl,  $\text{R}_2$  is H or  $-(\text{CH}_2)_n\text{CH}=\text{CH}_2$ , where  $n$  is in the range of from about 1 to about 50,  $\text{R}_3$  and  $\text{R}_4$  are independently selected from methyl, ethyl, propyl and phenyl,  $\text{R}$  is an end-gap, such as an optionally hydroxy-substituted alkyl group having from 1 to 50 carbon atoms, preferably an alkyl group having from 1 to 5 carbon atoms, more preferably an alkyl group having 1 or 2 carbon atoms,  $p$  is an integer in the range of from about 1 to about 2000, preferably from about 1 to about 500,  $q$  is an integer in the range of from about 1 to about 1000, preferably from about 1 to about 500.

In preferred embodiments the polyorganosiloxane is selected from polymers having the following general structure:



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $p$  and  $q$  are as defined above.

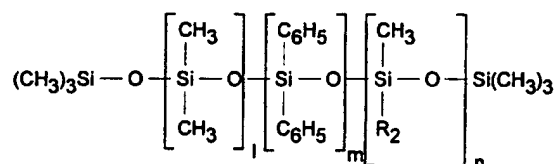
As defined herein,  $p$  and  $q$  reflect the number of Si-O linkages in the polymer chain and  $\text{R}_1$  and  $\text{R}_2$  and  $\text{R}_3$  and  $\text{R}_4$  may vary going from one monomer unit to the next. For example, suitable polyorganosiloxane polymers for use herein include methyl vinyl dimethicone, methyl vinyl diphenyl dimethicone and methyl vinyl phenyl methyl diphenyl dimethicone.

In order to achieve crosslinking between the polyorganosiloxane polymer and the crosslinking agent, an (-Si-H) group must crosslink with a

-Si-( $\text{CH}_2$ ) $_n$ CH=CH $_2$  group, so that for any specific crosslink, the group  $\text{R}_2$  must be different in the polyorganosiloxane polymer and the crosslinking agent. For example, for any specific crosslink, when  $\text{R}_2$  is

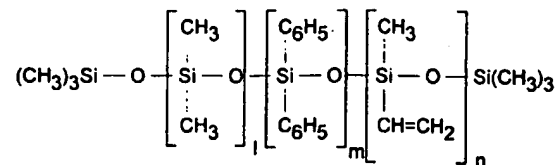
-( $\text{CH}_2$ ) $_n$ CH=CH $_2$  in the polyorganosiloxane polymer,  $\text{R}_2$  must be H in the crosslinking agent, and vice versa. However, there can be mixtures of  $\text{R}_2$  for each of the polyorganosiloxane polymer and crosslinking agent.

In preferred embodiments, the polyorganosiloxane polymer is selected from an alkylarylpolysiloxane polymer having the general formula:



wherein  $\text{R}_2$  is selected from -CH=CH $_2$  or H, preferably -CH=CH $_2$ , and wherein  $l$  is an integer in the range of from about 1 to about 1000, preferably from about 1 to about 500,  $m$  is an integer in the range from 0 to about 1000, preferably from about 0 to about 500, and  $n$  is an integer in the range of from about 1 to about 1000, preferably from about 1 to about 100.

In particularly preferred embodiments the polyorganosiloxane polymer is selected from an alkylarylpolysiloxane polymer having the general formula:



wherein l, m and n are as defined above. In preferred embodiments m is in the range of from about 1 to about 1000, preferably from about 200 to about 800.

The first silicone-containing phase also comprises a silicone oil. Any straight chain, branched and cyclic silicones suitable for use in skin care compositions can be used herein. The silicone oils can be volatile or non-volatile. Suitable silicone oils for use herein include silicone oils having a weight average molecular weight of about 100,000 or less, preferably about 50,000 or less. Preferably the silicone oil is selected from silicone oils having a weight average molecular weight in the range from about 100 to about 50,000, and preferably from about 200 to about 40,000. In preferred embodiments, the silicone oil is selected from dimethicone, decamethylcyclopentasiloxane, octamethylcyclotetrasiloxane and phenyl methicone, and mixtures thereof, most preferably phenyl methicone.

Suitable materials for use in the first silicone-containing phase are available under the tradename KSG supplied by Shinetsu Chemical Co., Ltd, for example KSG-15, KSG-16, KSG-17, KSG-18. These materials contain a combination of crosslinked polyorganosiloxane polymer and silicone oil. Particularly preferred for use herein especially in combination with the organic amphiphilic emulsifier material is KSG-18. The assigned INCI names for KSG-15, KSG-16, KSG-17 and KSG-18 are Cyclomethicone Dimethicone/Vinyl Dimethicone Crosspolymer, Dimethicone Dimethicone/Vinyl Dimethicone Crosspolymer, Cyclomethicone Dimethicone/Vinyl Dimethicone Crosspolymer and Phenyl Trimethicone Dimethicone/Phenyl Vinyl Dimethicone Crosspolymer, respectively.

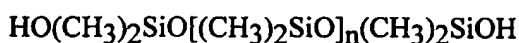
Compositions herein preferably also comprise a second non-crosslinked silicone-containing phase. In preferred embodiments the second silicone-containing phase is present in a level of from about 0.1% to about 20%, especially from about 0.1% to about 10% by weight of composition.

Suitable silicone fluids for use in the second silicone-containing phase herein include water-insoluble silicones inclusive of non-volatile polyalkyl and polyaryl siloxane gums and fluids, volatile cyclic and linear polyalkylsiloxanes, polyalkoxylated silicones, amino and quaternary ammonium modified silicones, and mixtures thereof.

In preferred embodiments the second silicone-containing phase comprises a silicone gum or a mixture of silicones including the silicone gum. As used herein, the term "silicone gum" means high molecular weight silicone-based fluids having a mass-average molecular weight in excess of about 200,000 and preferably from about 200,000 to about 400,000. Silicone oils generally have a molecular weight of less than about 200,000. Typically, silicone gums have a viscosity at 25°C in excess of about 1,000,000 mm<sup>2</sup>.s<sup>-1</sup>. The silicone gums include dimethicones as described by Petrarch and others including US-A-4,152,416, May 1, 1979 to Spitzer, et al, and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76.

Silicone gums for use herein include any silicone gum suitable for use in a skin care composition. Suitable silicone gums for use herein are silicone gums having a molecular weight of from about 200,000 to about 4,000,000 selected from dimethiconol, fluorosilicone and dimethicone and mixtures thereof.

Dimethiconol-based silicones suitable for use herein can have the chemical structure (II):



where n is from about 2000 to about 40,000, preferably from about 3000 to about 30,000.

Exemplary fluorosilicones useful herein can have a molecular weight of from about 200,000 to about 300,000, preferably from about 240,000 to about 260,000 and most preferably about 250,000.

Specific examples of silicone gums include polydimethylsiloxane, (polydimethylsiloxane)(methylvinylsiloxane) copolymer, poly(dimethylsiloxane)(diphenyl)(methylvinylsiloxane) copolymer and mixtures thereof.

The silicone gum used herein can be incorporated into the composition as part of a mixture of silicones. When the silicone gum is incorporated as part of a mixture of silicones, the silicone gum preferably constitutes from about 5% to about 40%, especially from about 10% to 20% by weight of the silicone mixture. The silicone or silicone mixture preferably constitutes from about 0.1% to about 20%, more preferably from about 0.1% to about 15%, and especially from about 0.1% to about 10% by weight of composition.

Suitable silicone gum-based silicone mixtures for use in the second silicone-containing phase of the compositions herein include mixtures consisting essentially of:

- (i) a silicone having a molecular weight of from about 200,000 to about 4,000,000 selected from dimethiconol, fluorosilicone and dimethicone and mixtures thereof; and
- (ii) a silicone-based carrier having a viscosity from about  $0.65 \text{ mm}^2 \cdot \text{s}^{-1}$  to about  $100 \text{ mm}^2 \cdot \text{s}^{-1}$ ,

wherein the ratio of i) to ii) is from about 10:90 to about 20:80 and wherein said silicone gum-based component has a final viscosity of from about  $500 \text{ mm}^2 \cdot \text{s}^{-1}$  to about  $10,000 \text{ mm}^2 \cdot \text{s}^{-1}$ .

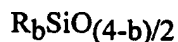
The silicone-based carriers suitable for use herein include certain silicone fluids. The silicone fluid can be either a polyalkyl siloxane, a polyaryl siloxane, a polyalkylaryl siloxane or a polyether siloxane copolymer. Mixtures of these fluids can also be used and are preferred in certain executions.

The polyalkyl siloxane fluids that can be used include, for example, polydimethylsiloxanes with viscosities ranging from about  $0.65$  to  $600,000 \text{ mm}^2 \cdot \text{s}^{-1}$ , preferably from about  $0.65$  to about  $10,000 \text{ mm}^2 \cdot \text{s}^{-1}$  at  $25^\circ\text{C}$ . These siloxanes are available, for example, from the General Electric Company as the Viscasil (RTM) series and from Dow Corning as the Dow Corning 200 series. The essentially non-volatile polyalkylarylsiloxane fluids that can be used include, for example, polymethylphenylsiloxanes, having viscosities of about  $0.65$  to  $30,000 \text{ mm}^2 \cdot \text{s}^{-1}$  at  $25^\circ\text{C}$ . These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid. Also suitable for use herein are certain volatile cyclic polydimethylsiloxanes having a ring structure incorporating from about 3 to about 7  $(\text{CH}_3)_2\text{SiO}$  moieties.

The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 29, 1970. Preferably the viscosity of the silicone blend constituting the second fluid phase ranges from about  $500 \text{ mm}^2.\text{s}^{-1}$  to about  $100,000 \text{ mm}^2.\text{s}^{-1}$ , preferably from about  $1000 \text{ mm}^2.\text{s}^{-1}$  to about  $10,000 \text{ mm}^2.\text{s}^{-1}$ .

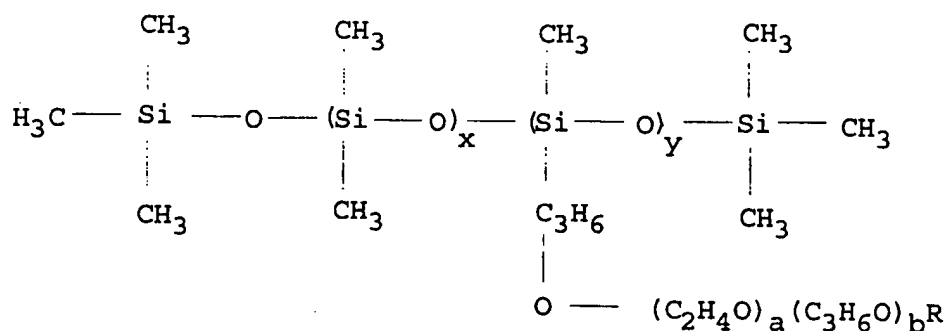
An especially preferred silicone-gum based component for use in the compositions herein is a dimethiconol gum having a molecular weight of from about 200,000 to about 4,000,000 along with a silicone carrier with a viscosity of about 0.65 to  $100 \text{ mm}^2.\text{s}^{-1}$ . An example of this silicone component is Dow Corning Q2-1403 (85%  $5 \text{ mm}^2.\text{s}^{-1}$  Dimethicone Fluid/15% Dimethiconol) and Dow Corning Q2-1401 available from Dow Corning.

Another class of silicone suitable for use in the second silicone-containing phase herein include polydiorganosiloxane-polyoxyalkylene copolymers containing at least one polydiorganosiloxane segment and at least one polyoxyalkylene segment, said polydiorganosiloxane segment consisting essentially of



siloxane units wherein b has a value of from about 0 to about 3, inclusive, there being an average value of approximately 2 R radicals per silicon for all siloxane units in the copolymer, and R denotes a radical selected from methyl, ethyl, vinyl, phenyl and a divalent radical bonding said polyoxyalkylene segment to the polydiorganosiloxane segment, at least about 95% of all R radicals being methyl; and said polyoxyalkylene segment having an average molecular weight of at least about 1000 and consisting of from about 0 to about 50 mol percent polyoxypropylene units and from about 50 to about 100 mol percent polyoxyethylene units, at least one terminal portion of said polyoxyalkylene segment being bonded to said polydiorganosiloxane segment, any terminal portion of said polyoxyalkylene segment not bonded to said polydiorganosiloxane segment being satisfied by a terminating radical; the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in said copolymer having a value of from about 2 to about 8. Such polymers are described in US-A-4,268,499.

Preferred for use herein are polydiorganosiloxane-polyoxyalkylene copolymers having the general formula:



wherein x and y are selected such that the weight ratio of polydiorgano-siloxane segments to polyoxalkalkylene segments is from about 2 to about 8, the mol ratio of a:(a+b) is from about 0.5 to about 1, and R is a chain terminating group, especially selected from hydrogen; hydroxyl; alkyl, such as methyl, ethyl, propyl, butyl, benzyl; aryl, such as phenyl; alkoxy such as methoxy, ethoxy, propoxy, butoxy; benzyloxy; aryloxy, such as phenoxy; alkenyloxy, such as vinyloxy and allyloxy; acyloxy, such as acetoxy, acryloxy and propionoxy and amino, such as dimethylamino.

The number of and average molecular weights of the segments in the copolymer are such that the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in the copolymer is preferably from about 2.5 to about 4.0.

Suitable copolymers are available commercially under the tradenames Belsil (RTM) from Wacker-Chemie GmbH, Geschäftsbereich S, Postfach D-8000 Munich 22 and Abil (RTM) from Th. Goldschmidt Ltd., Tego House, Victoria Road, Ruislip, Middlesex, HA4 0YL, for example Belsil (RTM) 6031 and Abil (RTM) B88183. A particularly preferred copolymer for use herein includes Dow Corning DC3225C which has the CTFA designation Dimethicone/Dimethicone copolyol.

In preferred embodiments, a third oil phase is present in an amount of from about 0.1% to about 15%, more preferably from about 1% to about 10% by weight of composition. The third oil phase can be either a separate phase or can form one phase together with either or both of the first and second silicone phases. Preferably, the third oil phase is a separate phase.

The third oil phase preferably comprises a non-silicone organic oil, such as a natural or synthetic oil selected from mineral, vegetable, and animal oils, fats and waxes, fatty acid esters, fatty alcohols, fatty acids and mixtures thereof, which ingredients are useful for achieving emollient cosmetic properties. The first oil phase component is preferably essentially silicone-free, i.e., it contains no more than about

10%, preferably no more than about 5% by weight of silicone-based materials. It will be understood that the oil phase may contain, for example, up to about 25%, preferably up to only about 10% of oil phase soluble emulsifier ingredients. Such ingredients are not to be considered as oil phase components from the viewpoint of determining the oil phase level and required HLB. In preferred embodiments, the overall required HLB of the oil phase is from about 8 to about 12, especially from about 9 to about 11, required HLB being determined by summing the individual required HLB values for each component of the oil phase multiplied by its W/W percentage in the oil phase (see ICI Literature on HLB system; ICI reference paper ref 51/0010/303/15m., first printed in 1976, revised in 1984 and May 1992).

Suitable first oil phase components for use herein include, for example, optionally hydroxy-substituted C<sub>8</sub>-C<sub>50</sub> unsaturated fatty acids and esters thereof, beeswax, saturated and unsaturated fatty alcohols such as behenyl alcohol and cetyl alcohol, hydrocarbons such as mineral oils, petrolatum and squalane, fatty sorbitan esters (see US-A-3988255, Seiden, issued October 26 1976), lanolin and lanolin derivatives, animal and vegetable triglycerides such as almond oil, peanut oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, shea butter, shorea butter, and sunflower seed oil and C<sub>1</sub>-C<sub>24</sub> esters of dimer and trimer acids such as diisopropyl dimerate, diisostearylmalate, diisostearyldimerate and triisostearyltrimerate. Of the above, highly preferred are the mineral oils, petrolatums, unsaturated fatty acids and esters thereof and mixtures thereof.

Preferred embodiments herein comprise from about 0.1% to about 10% by weight of an unsaturated fatty acid or ester. Preferred unsaturated fatty acids and esters for use herein are optionally hydroxy substituted C<sub>8</sub>-C<sub>50</sub> unsaturated fatty acids and esters, especially esters of ricinoleic acid. The unsaturated fatty acid or ester component is valuable herein in combination with the liquid crystal-forming emulsifier for improving the skin feel and rub-in characteristics of the composition. Highly preferred in this respect is cetyl ricinoleate.

#### Amphiphilic Surfactant

A further preferred component of the compositions herein is an organic amphiphilic surfactant which is capable of forming smectic lyotropic crystals in product or when the product is being applied to the skin at ambient or elevated temperatures.

Preferably the amphiphilic surfactant is capable of forming liquid crystals at a temperature in the range from about 20°C to about 40°C. Preferably the amphiphilic surfactant is capable of forming smectic lyotropic liquid crystals. Once application of the product to the skin has been completed, liquid crystals may not be identifiable on the skin surface or stratum corneum. The amphiphilic surfactant is preferably present at a level of from about 0.1% to about 20%, preferably from about 0.1% to about 10%, by weight.

The liquid-crystal forming amphiphilic surfactants suitable for use herein contain both hydrophilic and lipophilic groupings and exhibit a marked tendency to adsorb at a surface or interface, i.e. they are surface-active. Amphiphilic surface-active materials for use herein include nonionic (no charge), anionic (negative charge), cationic (positive charge) and amphoteric (both charges) based on whether or not they ionize in aqueous media.

In the literature, liquid crystals are also referred to as anisotropic fluids, a fourth state of matter, surfactant association structure or mesophases. Those terms are often used interchangeably. The term "lyotropic" means a liquid crystalline system containing a polar solvent, such as water. The liquid crystals used herein are preferably lamellar, hexagonal, rod or vesicle structures or mixtures thereof.

The liquid crystalline phase utilized in the compositions of the invention can be identified in various ways. A liquid crystal phase flows under shear and is characterised by a viscosity that is significantly different from the viscosity of its isotropic solution phase. Rigid gels do not flow under shear like liquid crystals. Also, when viewed with a polarized light microscope, liquid crystals show identifiable birefringence, as, for example, planar lamellar birefringence, whereas when isotropic solutions and rigid gels are viewed under polarized light, both show dark fields.

Other suitable means for identifying liquid crystals include X-ray diffraction, NMR spectroscopy and transmission electron microscopy.

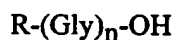
In general terms, the organic amphiphilic surfactant preferred for use herein can be described as a liquid, semi-solid or waxy water-dispersible material having the formula X-Y where X represents a hydrophilic, especially nonionic moiety and Y represents a lipophilic moiety.

Organic amphiphilic surfactants suitable for use herein include those having a weight average HLB (Hydrophilic Lipophilic Balance) in the range from about 2 to about 12, preferably from about 4 to about 8.

Preferred organic amphiphilic surfactants employed herein have a long saturated or unsaturated branched or linear lipophilic chain having from about 12 to about 30 carbon atoms such as oleic, lanolic, tetradecylic, hexadecylic, isostearyl, lauric, coconut, stearic or alkyl phenyl chains. When the hydrophilic group of the amphiphilic material forming the liquid crystal phase is a nonionic group, a polyoxyethylene, a polyglycerol, a polyol ester, oxyalkylated or not, and, for example, a polyoxyalkylated sorbitol or sugar ester, can be employed. When the hydrophilic group of the amphiphilic surfactant forming the liquid crystal phase is an ionic group, advantageously there can be used, as the hydrophilic group, a phosphatidylcholine residue as found in lecithin.

Hydrophilic moieties suitable for use herein are selected from:

- (1) ethers of linear, or branched, polyglycerol having the following formula:



wherein  $n$  is a whole number between 1 and 6,  $R$  is selected from aliphatic, linear or branched, saturated or unsaturated chains of 12 to 30 carbon atoms, the hydrocarbon radicals of lanolin alcohols and the 2-hydroxy alkyl residue of long chain, alpha-diols, and Gly represents a glycerol residue;

- (2) polyethoxylated fatty alcohols, for example those of the formula  $R^1(C_2R_4O)_x\text{OH}$  wherein  $R^1$  is  $C_{12}$ - $C_{30}$  linear or branched alkyl or alkenyl and  $x$  averages from about 0 to about 20, preferably from about 0.1 to about 6, more preferably from about 1 to about 4;
- (3) polyol esters and polyalkoxylated polyol esters, and mixtures thereof, the polyols preferably being selected from sugars,  $C_2$ - $C_6$  alkylene glycols, glycerol, polyglycerols, sorbitol, sorbitan, polyethylene glycols and polypropylene glycols and wherein the polyalkoxylated polyol esters contain from about 2 to about 20 preferably from about 2 to about 4 moles of alkylene oxide (especially ethylene oxide) per mole of polyol ester;
- (4) natural and synthetic phosphoglycerides, glycolipids and sphingolipids, for example cerebrosides, ceramides and lecithin.

Examples of amphiphilic surfactants suitable for use herein include C<sub>8</sub>-C<sub>30</sub> alkyl and acyl-containing amphoteric, anionic, cationic and nonionic surfactants as set out below.

#### Amphoteric

N-alkyl amino acids (e.g., sodium N-alkylaminoacetate);  
N-lauroylglutamic acid cholesterol ester (e.g., Eldew CL-301 Ajinomoto)

#### Anionic

Acylglutamates (e.g., disodium N-lauroylglutamate);  
Sarcosinates (e.g., sodium lauryl sarcosinate. Grace, Seppic);  
Taurates (e.g., sodium lauryl taurate. sodium methyl cocoyl taurate);  
Carboxylic acids and salts (e.g., potassium oleate; potassium laurate; potassium-10-undecenoate; potassium 11-(p-styryl) - undecanoate);  
Ethoxylated carboxylic salts (e.g., sodium carboxy methyl alkyl ethoxylate);  
Ether carboxylic acids;  
Phosphoric acid esters and salts (e.g., lecithin; DEA-oleth-10 phosphate);  
Acyl isethionates (e.g., sodium 2-lauroyloxyethane sulfonate);  
Alkane sulfonates (e.g., branched sodium x-alkane sulfonate (x/1);  
Sulfosuccinates e.g.,  
    Sodium dibutyl sulfosuccinate,  
    Sodium di-2-pentyl sulfosuccinate,  
    Sodium di-2-ethylbutyl sulfosuccinate,  
    Sodium di-hexyl-sulfosuccinate,  
    Sodium di-2 ethylhexyl sulfosuccinate (AOT),  
    Sodium di-2-ethyldodecyl sulfosuccinate,  
    Sodium di-2-ethyloctadecyl sulfosuccinate,  
    Dioctyl sodium sulfosuccinate,  
    Disodium laureth sulfosuccinate (MacKanate El, McIntyre Group Ltd.)  
Sulfuric acid esters (e.g., sodium 2-ethylhept-6-enyl sulfate; sodium 11-heneicosyl sulfate; sodium 9-heptadecyl sulfate).  
Alkyl sulfates (e.g., MEA alkyl sulfate such as MEA-lauryl sulfate)

#### Cationic

Alkyl Imidazolines (e.g., alkyl hydroxyethyl imidazoline, stearyl hydroxyethyl imidazoline (supplier Akzo, Finetex and Hoechst));

Ethoxylated Amines (e.g., PEG-n alkylamine, PEG-n alkylamino propylamine, Poloxamine, PEG-cocopolyamine, PEG-15 tallow amine);

Alkylamines (e.g., dimethyl alkylamine; dihydroxyethyl alkylamine dioleate)

#### Quaternaries:

Alkylbenzyl dimethylammonium salts (e.g., stearalkonium chloride);  
Alkyl betaines (e.g., dodecyl dimethyl ammonio acetate, oleyl betaine);  
Heterocyclic ammonium salts (e.g., alkylethyl morpholinium ethosulfate);

Tetraalkylammonium salts (e.g., dimethyl distearyl quaternary ammonium chloride (Witco));

Bis-isostearamidopropyl hydroxypropyl diammonium chloride (Schercoquat 21AP from Scher Chemicals);

1.8-Bis (decyldimethylammonio)-3, 6 dioxaoctane ditosylate

#### Nonionic Surfactants

Ethoxylated glycerides;

Monoglycerides (e.g., monoolein; monolinolein; monolaurin; 1-dodecanoyl-glycerol monolaurin; 1, 13-docosenoyl-glycerol monoerucin

diglyceride fatty acid (e.g., diglycerol monoisostearate Cosmol 41, fractionated. Nisshin Oil Mills Ltd.);

Polyglyceryl esters (e.g., triglycerol monooleate (Grindsted TS-T122), diglycerol monooleate (Grindsted TST-T101);

Polyhydric alcohol esters and ethers (e.g., sucrose cocoate, cetostearyl glucoside (Montanol, Seppic),  $\beta$  octyl glucofuranoside esters, alkyl glucoside such C<sub>10</sub>-C<sub>16</sub> (Henkel));

Diesters of phosphoric acid (e.g., sodium dioleoyl phosphate);

Alkylamido propyl betaine (e.g., cocoamido propyl betaine);

Amide: (e.g., N-(dodecanoylaminoethyl)-2-pyrrolidone);

Amide oxide: e.g., 1, 1 Dihydroperfluorooctyldimethylamine oxide,  
Dodecyldimethylamine oxide,  
2-Hydroxydodecyldimethylamine oxide,  
2-Hydroxydodecyl-bis (2-hydroxyethyl) amine oxide,  
2-Hydroxy-4-oxahexadecyldimethylamine oxide,

Ethoxylated amides (e.g., PEG-n acylamide);

Ammonio phosphates (e.g., didecanoyl lecithin);

Amine (e.g., octylamine);

Ammonio amides e.g.,

N-trimethylammoniodecanamidate,

N-trimethylammoniododecanamidate,

Ammonio carboxylates e.g.,

dodecyldimethylammonioacetate,

6-didodecylmethylammoniohexanoate,

Phosphonic and phosphoric esters and amides e.g.,

methyl-N-methyl-dodecylphosphonamidate,

dimethyl dodecylphosphonate,

dodecyl methyl methylphosphonate,

N,N-dimethyl dodecylphosphonic diamide

Ethoxylated alcohols

Polyoxyethylene (C<sub>8</sub>) e.g.,

pentaoxyethylene glycol p-n-octylphenyl ether

hexaoxyethylene glycol p-n-octylphenyl ether

nonaoxyethylene glycol p-n-octylphenyl ether

Polyoxyethylene (C<sub>10</sub>) e.g.,

pentaoxyethylene glycol p-n-decylphenyl ether,  
 decyl glyceryl ether, 4-oxatetradecan-1, 2-diol,  
 nonaoxyethylene glycol p-n-decylphenyl ether  
 Polyoxyethylene (C<sub>11</sub>) e.g.,  
     Tetraoxyethylene glycol undecyl ether  
 Polyoxyethylene (C<sub>12</sub>) e.g.,  
     3, 6, 9, 13-tetraoxapentacosan 1, 11-diol,  
     3, 6, 10-trioxadocosan-1, 8-diol,  
     3, 6, 9, 12, 16-pentaooxaoctacosan 1, 14-diol,  
     3,6,9,12,15-pentaooxanonacosan-1, 17-diol,  
     3, 7-dioxanonadecan-1, 5-diol,  
     3, 6, 12, 15, 19-hexaoxahentriacontan-1, 16-diol,  
     pentaoxyethylene glycol dodecyl ether,  
     monaoxyethylene glycol p-n-dodecylphenyl ether,  
 Polyoxyethylene(C<sub>14</sub>) e.g.,  
     3, 6, 9, 12, 16-pentaooxaoctacosan-1, 14-diol,  
     3, 6, 9, 12,15,19-heraoxatriacontan-1, 17-diol,  
 Sulfone diimines e.g.,  
     decyl methyl sulfone diimine  
 Sulfoxides e.g.,  
     3-decyloxy-2-hydroxypropyl methyl sulfoxide  
     4-decyloxy-3-hydroxybutyl methyl sulfoxide  
 Sulfoximines e.g.,  
     N-methyl dodecyl methyl sulfoximine

Preferred organic amphiphilic surfactants for use herein are nonionic amphiphilic surfactants having a hydrophilic moiety selected from polyol esters and polyalkoxylated polyol esters, and mixtures thereof, the polyols preferably being selected from sugars, C<sub>2</sub>-C<sub>6</sub> alkylene glycols, glycerol, polyglycerols, sorbitol, sorbitan, polyethylene glycols and polypropylene glycols and wherein the polyalkoxylated polyol esters contain from about 2 to about 20 preferably from about 2 to about 4 moles of alkylene oxide (especially ethylene oxide) per mole of polyol ester, and a lipophilic moiety selected from long saturated or unsaturated branched chain or linear lipophilic chains having from about 12 to about 30 carbon atoms such as oleic, lanolic, tetradecylic, hexadecylic, isostearyl, lauric, coconut, stearic or alkyl phenyl chains.

Highly preferred organic amphiphilic surfactants for use herein are selected from polyhydric alcohol esters and ethers. Especially preferred amphiphilic surfactants for use herein are sugar esters and polyalkoxylated sugar esters.

The sugar esters for use in this invention can be classified as hydrocarbyl and alkyl polyoxyalkylene esters of cyclic polyhydroxy saccharides wherein one or more of the hydroxyl groups on the saccharide moiety is substituted with an acyl or polyoxyalkylene group. Hydrocarbyl sugar esters can be prepared in well-known fashion by heating an acid or acid halide with sugar, i.e., by a simple esterification reaction.

The sugars employed in the preparation of the sugar esters include monosaccharides, di-saccharides and oligo-saccharides well known in the art, for example, the dextrorotatory and levorotatory forms of glucose, fructose, mannose, galactose, arabinose and xylose. Typical di-saccharides include maltose, cellobiose, lactose, and trehalose. Typical tri-saccharides include raffinose and gentianose. The di-saccharides are preferred for use herein, especially sucrose.

Sucrose can be esterified at one or more of its eight hydroxyl groups to provide the sucrose esters useful herein. When sucrose is combined with an esterification agent in a 1:1 mole ratio, sucrose monoesters are formed; when the ratio of esterification agent to sucrose is 2:1, or greater, the di-, tri-, etc., esters are formed, up to a maximum of the octa-ester.

Preferred sugar esters herein are those prepared by the esterification of sugars at a mole ratio of esterification agent:sugar of 1:1 and 3:1 i.e., the mono-acyl and di- or higher acyl sugar esters. Especially preferred are the mono-, di- and tri-acyl sugar esters and mixtures thereof wherein the acyl substituents contain from about 8 to about 24, preferably from about 8 to about 20 carbon atoms and 0,1 or 2 unsaturated moieties. Of the mono-acyl and di-acyl sugar esters, the respective esters of di-saccharide sugars, especially sucrose, wherein the acyl groups contain from about 8 to about 20 carbon atoms are especially preferred. Preferred sugar esters herein are sucrose cocoate, sucrose monooctanoate, sucrose monodecanoate, sucrose monolaurate, sucrose monomyristate, sucrose monopalmitate, sucrose monostearate, sucrose monooleate, sucrose monolinoleate, sucrose dioleate, sucrose dipalmitate, sucrose distearate, sucrose dilaurate and sucrose dilinoleate, and mixtures thereof. Sucrose cocoate has been found to be particularly efficacious in the compositions herein. In mixtures of mono-acyl with di-, tri- and higher acyl sugar esters, the mono- and di-acyl esters preferably comprise at least about 40%, more preferably from about 50% to about 95% by weight of the total sugar ester mixture.

Other sugar esters suitable for use in the compositions of this invention are the alkyl polyoxyalkylene sugar esters wherein one hydroxyl group is substituted with a C<sub>8</sub>-C<sub>18</sub> alkyl group and wherein one or more of the hydroxyl groups on the sugar molecule are replaced by an ester or ether substituent containing the moiety  $[(CH_2)_x-O]_y$  wherein x is an integer from 2 to about 4, preferably 2, and wherein y is an integer from about 1 to about 50, preferably 8 to 30 polyoxyalkylene substituents. Especially preferred herein are sugar esters wherein the polyoxyalkylene substituent is a polyoxyethylene substituent containing from about 8 to about 30 polyoxyethylene groups. Such materials wherein sorbitan is the sugar moiety are commercially available under the tradename "Tweens". Such mixed esters can be prepared by first acylating a sugar at a 1:1 mole ratio with a hydrocarbyl acid halide followed by reaction with the corresponding polyoxyalkylene acid halide or alkylene oxide to provide the desired material. The simple polyoxyalkylene ester of di-saccharides, especially sucrose, wherein the polyoxyalkylene groups contain up to about 20 alkylene oxide moieties are another useful class of sugar esters herein. A preferred sugar ester of this class is sorbitol trioleate ethoxylated with 20 moles of ethylene oxide. Mixtures of sugar esters with other polyol esters, eg. glycerol esters, are also suitable for use herein, for example, Palm Oil Sucroglyceride (Rhône-Poulenc).

As used herein, the term "lecithin" refers to a material which is a phosphatide. Naturally occurring or synthetic phosphatides can be used. Phosphatidylcholine or lecithin is a glycerine esterified with a choline ester of phosphoric acid and two fatty acids, usually a long chain saturated or unsaturated fatty acid having 16-20 carbons and up to 4 double bonds. Other phosphatides capable of forming lamellar or hexagonal liquid crystals can be used in place of the lecithin or in combination with it. These phosphatides are glycerol esters with two fatty acids as in the lecithin, but the choline is replaced by ethanolamine (a cephalin), or serine (  $\alpha$ -aminopropanoic acid; phosphatidyl serine) or an inositol (phosphatidyl inositol). While the invention herein is exemplified with lecithin, it is understood that these other phosphatides can be used herein.

A variety of lecithins can be used. American Lecithin Company supplies a Nattermann Phospholipid, Phospholipan 80 and Phosal 75. Other lecithins which can be used alone or in combination with these are: Actifla Series, Centrocaps series, Central Ca, Centrol series, Centrolene, Centrolene, Centrolene, Centromix, Centrophase and Centrophil Series from Central Soya; Alcolac and Alcolac 439-C from American

Lecithin; Canaspersa from Canada Packers, Lexin K and Natipide from American Lecithin; and L-Clearate, Clearate LV and Clearate WD from the W.A. Cleary Co. Lecithins are supplied dissolved in ethanol, fatty acids, triglycerides and other solvents. They are usually mixtures of lecithins and range from 15% to 50% of the solution as supplied.

Both natural and synthetic lecithins can be used. Natural lecithins are derived from oilseeds such as sunflower seeds, soybeans, safflower seeds and cottonseed. The lecithins are separated from the oil during the refining process.

The organic amphiphilic surfactant has been found to be especially valuable herein for improving the stability and skin feel of the compositions of the invention.

The amphiphilic surfactant is preferably incorporated into the composition in an amount of from about 0.1 % to about 20% , preferably from about 0.1% to about 10%, and more preferably from about 0.1% to about 8% by weight of composition.

Highly preferred herein is a fatty acid ester blend based on a mixture of sorbitan or sorbitol fatty acid ester and sucrose fatty acid ester, the fatty acid in each instance being preferably C<sub>8</sub>-C<sub>24</sub>, more preferably C<sub>10</sub>-C<sub>20</sub>. The preferred fatty acid ester emulsifier from the viewpoint of moisturisation is a blend of sorbitan or sorbitol C<sub>16</sub>-C<sub>20</sub> fatty acid ester with sucrose C<sub>10</sub>-C<sub>16</sub> fatty acid ester, especially sorbitan stearate and sucrose cocoate. This is commercially available from ICI under the trade name Arlatone 2121.

A highly preferred ingredient of the compositions herein is urea which is preferably present in a level of from about 0.1% to about 20%, more preferably from about 0.5% to about 10% and especially from about 1% to about 5% by weight of composition.

In preferred embodiments, the oil phase and organic amphiphilic surfactant when present are premixed in water at a temperature above the Kraft Point of the organic amphiphilic surfactant (but preferably below about 60°C) to form a liquid crystal/oil in water dispersion prior to addition of the urea. The urea is found to be especially effective herein in combination with the amphiphilic emulsifier surfactant and the polyol fatty acid polyester for providing outstanding skin moisturisation and softening in the context of an oil-in-water skin care emulsion composition.

Moreover, it is surprisingly found that the urea is rendered more stable to hydrolytic degradation, thereby allowing an increase in compositional pH.

A wide variety of optional ingredients such as non-occlusive moisturizers, humectants, gelling agents, neutralizing agents, perfumes, colouring agents and surfactants, can be added to the skin compositions herein.

The compositions herein can comprise a humectant. Suitable humectants for use herein include sorbitol, propylene glycol, butylene glycol, hexylene glycol, ethoxylated glucose derivatives, hexanetriol, glycerine, glycine, hyaluronic acid, arginine, Ajidew (NaPCA), water-soluble polyglycerylmethacrylate lubricants and panthenols. A preferred humectant herein is glycerine (sometimes known as glycerol or glycerin). Chemically, glycerine is 1,2,3-propanetriol and is a product of commerce. One large source of the material is in the manufacture of soap. Glycerine is especially preferred in the compositions of the invention from the viewpoint of boosting moisturisation. Also preferred for use herein is butylene glycol. Particularly preferred from the viewpoint of boosting moisturisation is a combination of glycerine and urea.

In the present compositions, the humectant is preferably present at a level of from about 0.1% to about 20%, more preferably from about 1% to about 15%, and especially from about 5% to about 15% by weight of composition.

Suitable polyglycerylmethacrylate lubricants for use in the compositions of this invention are available under the trademark Lubrajel (RTM) from Guardian Chemical Corporation, 230 Marcus Blvd., Hauppauge, N.Y. 11787. In general, Lubrajels can be described as hydrates or clathrates which are formed by the reaction of sodium glycerate with a methacrylic acid polymer. Thereafter, the hydrate or clathrate is stabilized with a small amount of propylene glycol, followed by controlled hydration of the resulting product. Lubrajels are marketed in a number of grades of varying glycerate: polymer ratio and viscosity. Suitable Lubrajels include Lubrajel TW, Lubrajel CG and Lubrajel MS, Lubrajel WA, Lubrajel DV and so-called Lubrajel Oil.

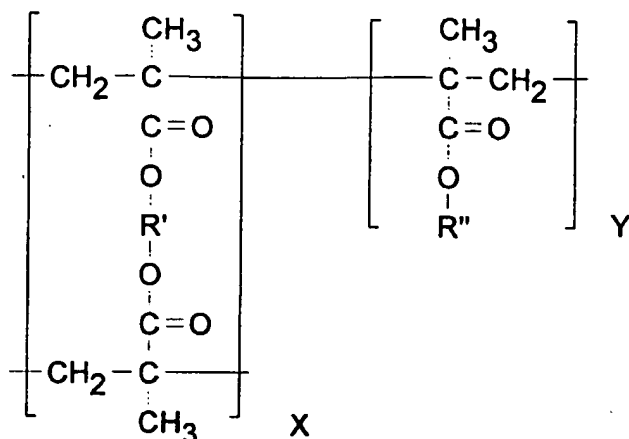
At least part (up to about 5% by weight of composition) of the humectant can be incorporated in the form of an admixture with a particulate lipophilic or hydrophobic

carrier material. The carrier material and humectant can be added either to the aqueous or disperse phase.

This copolymer is particularly valuable for reducing shine and controlling oil while helping to provide effective moisturization benefits. The cross-linked hydrophobic polymer is preferably in the form of a copolymer lattice with at least one active ingredient dispersed uniformly throughout and entrapped within the copolymer lattice. Alternatively, the hydrophobic polymer can take the form of a porous particle having a surface area ( $N_2$ , BET) in the range from about 50 to 500, preferably 100 to 300  $m^2.g^{-1}$  and having the active ingredient absorbed therein.

The cross-linked hydrophobic polymer is preferably present in an amount of from about 0.1% to about 10% by weight and is preferably incorporated in the external aqueous phase. The active ingredient can be one or more or a mixture of skin compatible oils, skin compatible humectants, emollients, moisturizing agents and sunscreens. In one embodiment, the polymer material is in the form of a powder, the powder being a combined system of particles. The system of powder particles forms a lattice which includes unit particles of less than about one micron in average diameter, agglomerates of fused unit particles of sized in the range of about 20 to 100 microns in average diameter and aggregates of clusters of fused agglomerates of sizes in the range of about 200 to 1,200 microns in average diameter.

The powder material of this embodiment can be broadly described as a cross-linked "post absorbed" hydrophobic polymer lattice. The powder preferably has entrapped and dispersed therein, an active which may be in the form of a solid, liquid or gas. The lattice is in particulate form and constitutes free flowing discrete solid particles when loaded with the active material. The lattice may contain a predetermined quantity of the active material. A suitable polymer has the structural formula:



where the ratio of x to y is 80:20, R' is  $-\text{CH}_2\text{CH}_2-$  and R'' is  $-(\text{CH}_2)_{11}\text{CH}_3$ .

The hydrophobic polymer is a highly crosslinked polymer, more particularly a highly cross-linked polymethacrylate copolymer. The material is manufactured by the Dow Corning Corporation, Midland, Michigan, USA, and sold under the trademark POLYTRAP (RTM). It is an ultralight free-flowing white powder and the particles are capable of absorbing high levels of lipophilic liquids and some hydrophilic liquids while at the same time maintaining a free-flowing powder character. The powder structure consists of a lattice of unit particles less than one micron that are fused into agglomerates of 20 to 100 microns and the agglomerates are loosely clustered into macro-particles or aggregates of about 200 to about 1200 micron size. The polymer powder is capable of containing as much as four times its weight of fluids, emulsions, dispersion or melted solids.

Adsorption of actives onto the polymer powder can be accomplished using a stainless steel mixing bowl and a spoon, wherein the active is added to the powder and the spoon is used to gently fold the active into the polymer powder. Low viscosity fluids may be adsorbed by addition of the fluids to a sealable vessel containing the polymer and then tumbling the materials until a consistency is achieved. More elaborate blending equipment such as ribbon or twin cone blenders can also be employed. The preferred active ingredient for use herein is glycerine. Preferably, the weight ratio of humectant : carrier is from about 1:4 to about 3:1.

Also suitable as a highly cross-linked polymethacrylate copolymer is Microsponges 5647. This takes the form of generally spherical particles of cross-linked hydrophobic polymer having a pore size of from about 0.01 to about 0.05  $\mu\text{m}$  and a

surface area of 200-300m<sup>2</sup>/g. Again, it is preferably loaded with humectant in the levels described above.

The compositions of the invention can also contain a hydrophilic gelling agent at a level preferably from about 0.01% to about 10%, more preferably from about 0.02% to about 2%, and especially from about 0.02% to about 0.5%. The gelling agent preferably has a viscosity (1% aqueous solution, 20°C, Brookfield RVT) of at least about 4000 mPa.s, more preferably at least about 10,000 mPa.s and especially at least 50,000 mPa.s.

Suitable hydrophilic gelling agents can generally be described as water-soluble or colloiddally water-soluble polymers, and include cellulose ethers (e.g. hydroxyethyl cellulose, methyl cellulose, hydroxypropylmethyl cellulose), polyvinylpyrrolidone, polyvinylalcohol, guar gum, hydroxypropyl guar gum and xanthan gum.

Preferred hydrophilic gelling agents herein, however, are acrylic acid/ethyl acrylate copolymers and the carboxyvinyl polymers sold by the B.F. Goodrich Company under the trade mark of Carbopol resins. These resins consist essentially of a colloiddally water-soluble polyalkenyl polyether crosslinked polymer of acrylic acid crosslinked with from 0.75% to 2.00% of a crosslinking agent such as for example polyallyl sucrose or polyallyl pentaerythritol. Examples include Carbopol 934, Carbopol 940, Carbopol 950, Carbopol 954, Carbopol 980, Carbopol 951 and Carbopol 981. Carbopol 934 is a water-soluble polymer of acrylic acid crosslinked with about 1% of a polyallyl ether of sucrose having an average of about 5.8 allyl groups for each sucrose molecule. A most preferred polymer is Carbopol 954. Also suitable for use herein are hydrophobically-modified cross-linked polymers of acrylic acid having amphipathic properties available under the Trade Name Carbopol 1382, Carbopol 1342 and Pemulen TR-1 (CTFA Designation: Acrylates/10-30 Alkyl Acrylate Crosspolymer). A combination of the polyalkenyl polyether cross-linked acrylic acid polymer and the hydrophobically modified cross-linked acrylic acid polymer is also suitable and is preferred for use herein. The gelling agents herein are particularly valuable for providing excellent stability characteristics over both normal and elevated temperatures.

Neutralizing agents suitable for use in neutralizing acidic group containing hydrophilic gelling agents herein include sodium hydroxide, potassium hydroxide, ammonium hydroxide, monoethanolamine, diethanolamine and triethanolamine.

The compositions of the invention are in emulsion form and are preferably formulated so as to have a product viscosity of at least about 4,000 mPa.s and preferably in the range from about 4,000 to about 300,000 mPa.s, more preferably from about 8,000 to about 200,000 mPa.s and especially from about 10,000 to about 100,000 mPa.s and even more especially from about 10,000 to about 50,000 mPa.s (25°C, neat, Brookfield RVT Spindle No. 5).

The compositions of the invention can also contain from about 0.1% to about 10%, preferably from about 1% to about 5% of a panthenol moisturizer. The panthenol moisturizer can be selected from D-panthenol ([R]-2,4-dihydroxy-N-[3-hydroxypropyl]-3,3-dimethylbutamide), DL-panthenol, calcium pantothenate, royal jelly, panthetine, pantotheine, panthenyl ethyl ether, pangamic acid, pyridoxin, pantoyl lactose and Vitamin B complex. Highly preferred from the viewpoint of skin care and tack reduction is D-panthenol.

The compositions of the present invention can additionally comprise from about 0.001% to about 0.5%, preferably from about 0.002% to about 0.05%, more preferably from about 0.005% to about 0.02% by weight of carboxymethylchitin. Chitin is a polysaccharide which is present in the integument of lobsters and crabs and is a mucopolysaccharide having beta (1-4) linkages of N-acetyl-D-glucosamine. Carboxymethylchitin is prepared by treating the purified chitin material with alkali followed by monochloroacetic acid. It is sold commercially in the form of a dilute (approximately 0.1% to 0.5% by weight) aqueous solution under the name Chitin Liquid available from A & E Connock Ltd., Fordingbridge, Hampshire, England.

Other optional materials include keratolytic agents/desquamation agents such as salicylic acid; proteins and polypeptides and derivatives thereof; water-soluble or solubilizable preservatives preferably at a level of from about 0.1% to about 5%, such as Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, benzyl alcohol, EDTA, Euxyl (RTM) K400, Bromopol (2-bromo-2-nitropropane-1,3-diol) and phenoxypropanol; anti-bacterials such as Irgasan (RTM) and phenoxyethanol (preferably at levels of from 0.1% to about 5%); soluble or colloiddally-soluble moisturising agents such as hylaronic acid and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials, Portsmouth, VA, USA and described in USA-A-4,076,663; vitamins such as vitamin A, vitamin C, vitamin E

and vitamin K; alpha and beta hydroxyacids; aloe vera; sphingosines and phytosphingosines, cholesterol; skin whitening agents; N-acetyl cysteine; colouring agents; perfumes and perfume solubilizers and additional surfactants/emulsifiers such as fatty alcohol ethoxylates, ethoxylated polyol fatty acid esters, wherein the polyol can be selected from glycerine, propyleneglycol, ethyleneglycol, sorbitol, sorbitan, polypropyleneglycol, glucose and sucrose. Examples include glyceryl monohydroxy stearate and stearyl alcohol ethoxylated with an average of from 10 to 200 moles of ethyleneoxide per mole of alcohol and PEG-6 caprylic/capric glycerides.

Also useful herein are sunscreens agents. A wide variety of sunscreens agents are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology. Preferred among those sunscreens which are useful in the compositions of the instant invention are those selected from 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-t-butylidibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, Parsol MCX, Eusolex 6300, Octocrylene, Parsol 1789, and mixtures thereof.

Still other useful sunscreens are those disclosed in U.S. Patent No. 4,937,370, to Sabatelli, issued June 26, 1990; and U.S. Patent No. 4,999,186, to Sabatelli et al., issued March 12, 1991. The sunscreens agents disclosed therein have, in a single molecule, two distinct chromophore moieties which exhibit different ultra-violet radiation absorption spectra. One of the chromophore moieties absorbs predominantly in the UVB radiation range and the other absorbs strongly in the UVA radiation range. These sunscreens agents provide higher efficacy, broader UV absorption, lower skin penetration and longer lasting efficacy relative to conventional sunscreens. Especially preferred examples of these sunscreens include those selected from 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2,4-dihydroxybenzophenone, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4-hydroxydibenzoylmethane, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-N,N-(2-ethylhexyl)-

methyaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane, and mixtures thereof.

Generally, the sunscreens can comprise from about 0.5% to about 20% of the compositions useful herein. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF). SPF is a commonly used measure of photoprotection of a sunscreen against erythema. See Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978.

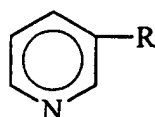
The compositions of the present invention can additionally comprise from about 0.1% to about 5% by weight of aluminium starch octenylsuccinate. Aluminium starch octenylsuccinate is the aluminium salt of the reaction product of octenylsuccinic anhydride with starch and is commercially available under the trade name from Dry Flo National Starch & Chemical Ltd. Dry Flo is useful herein from the viewpoint of skin feel and application characteristics.

Other optional materials herein include pigments which, where water-insoluble, contribute to and are included in the total level of oil phase ingredients. Pigments suitable for use in the compositions of the present invention can be organic and/or inorganic. Also included within the term pigment are materials having a low colour or lustre such as matte finishing agents, and also light scattering agents. Examples of suitable pigments are iron oxides, acyglutamate iron oxides, ultramarine blue, D&C dyes, carmine, and mixtures thereof. Depending upon the type of composition, a mixture of pigments will normally be used. The preferred pigments for use herein from the viewpoint of moisturisation, skin feel, skin appearance and emulsion compatibility are treated pigments. The pigments can be treated with compounds such as amino acids, silicones, lecithin and ester oils.

#### Vitamin B<sub>3</sub> component

The compositions of the present invention can also comprise a safe and effective amount of a vitamin B<sub>3</sub> compound. The compositions of the present invention preferably comprise from about 0.01% to about 50%, more preferably from about 0.1% to about 10%, even more preferably from about 0.5% to about 10%, and still more preferably from about 1% to about 5%, most preferably from about 2% to about 5%, of the vitamin B<sub>3</sub> compound.

As used herein, "vitamin B<sub>3</sub> compound" means a compound having the formula:

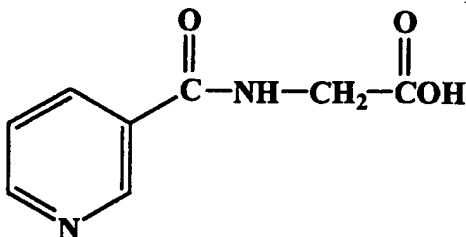


wherein R is - CONH<sub>2</sub> (i.e., niacinamide), - COOH (i.e., nicotinic acid) or - CH<sub>2</sub>OH (i.e., nicotinyl alcohol); derivatives thereof; and salts of any of the foregoing.

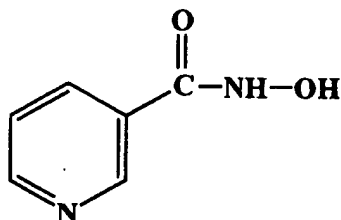
Exemplary derivatives of the foregoing vitamin B<sub>3</sub> compounds include nicotinic acid esters, including non-vasodilating esters of nicotinic acid, nicotinyl amino acids, nicotinyl alcohol esters of carboxylic acids, nicotinic acid N-oxide and niacinamide N-oxide.

Suitable esters of nicotinic acid include nicotinic acid esters of C<sub>1</sub>-C<sub>22</sub>, preferably C<sub>1</sub>-C<sub>16</sub>, more preferably C<sub>1</sub>-C<sub>6</sub> alcohols. The alcohols are suitably straight-chain or branched chain, cyclic or acyclic, saturated or unsaturated (including aromatic), and substituted or unsubstituted. The esters are preferably non-vasodilating. As used herein, "non-vasodilating" means that the ester does not commonly yield a visible flushing response after application to the skin in the subject compositions (the majority of the general population would not experience a visible flushing response, although such compounds may cause vasodilation not visible to the naked eye). Non-vasodilating esters of nicotinic acid include tocopherol nicotinate and inositol hexanicotinate; tocopherol nicotinate is preferred.

Other derivatives of the vitamin B<sub>3</sub> compound are derivatives of niacinamide resulting from substitution of one or more of the amide group hydrogens. Nonlimiting examples of derivatives of niacinamide useful herein include nicotinyl amino acids, derived, for example, from the reaction of an activated nicotinic acid compound (e.g., nicotinic acid azide or nicotinyl chloride) with an amino acid, and nicotinyl alcohol esters of organic carboxylic acids (e.g., C<sub>1</sub> - C<sub>18</sub>). Specific examples of such derivatives include nicotinuric acid (C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>) and nicotinyl hydroxamic acid (C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>), which have the following chemical structures: nicotinuric acid:



nicotinyl hydroxamic acid:



Exemplary nicotinyl alcohol esters include nicotinyl alcohol esters of the carboxylic acids salicylic acid, acetic acid, glycolic acid, palmitic acid and the like. Other non-limiting examples of vitamin B<sub>3</sub> compounds useful herein are 2-chloronicotinamide, 6-aminonicotinamide, 6-methylnicotinamide, n-methyl-nicotinamide, n,n-diethylnicotinamide, n-(hydroxymethyl)-nicotinamide, quinolinic acid imide, nicotinanilide, n-benzylnicotinamide, n-ethylnicotinamide, nifenazone, nicotinaldehyde, isonicotinic acid, methyl isonicotinic acid, thionicotinamide, nialamide, 1-(3-pyridylmethyl) urea, 2-mercaptonicotinic acid, nicomol, and niaprazine.

Examples of the above vitamin B<sub>3</sub> compounds are well known in the art and are commercially available from a number of sources, e.g., the Sigma Chemical Company (St. Louis, MO); ICN Biomedicals, Inc. (Irvin, CA) and Aldrich Chemical Company (Milwaukee, WI).

One or more vitamin B<sub>3</sub> compounds may be used herein. Preferred vitamin B<sub>3</sub> compounds are niacinamide and tocopherol nicotinate. Niacinamide is more preferred.

When used, salts, derivatives, and salt derivatives of niacinamide are preferably those having substantially the same efficacy as niacinamide in the methods of regulating skin condition described herein.

Salts of the vitamin B<sub>3</sub> compound can also be useful herein. Nonlimiting examples of salts of the vitamin B<sub>3</sub> compound useful herein include organic or inorganic salts, such as inorganic salts with anionic inorganic species (e.g., chloride, bromide, iodide, carbonate, preferably chloride), and organic carboxylic acid salts (including mono-, di- and tri- C1 - C18 carboxylic acid salts, e.g., acetate, salicylate, glycolate, lactate, malate, citrate, preferably monocarboxylic acid salts such as acetate). These and other salts of the vitamin B<sub>3</sub> compound can be readily prepared by the skilled

artisan, for example, as described by W. Wenner, "The Reaction of L-Ascorbic and D-Isoascorbic Acid with Nicotinic Acid and Its Amide", J. Organic Chemistry, VOL. 14, 22-26 (1949), which is incorporated herein by reference. Wenner describes the synthesis of the ascorbic acid salt of niacinamide.

In a preferred embodiment, the ring nitrogen of the vitamin B<sub>3</sub> compound is substantially chemically free (e.g., unbound and/or unhindered), or after delivery to the skin becomes substantially chemically free ("chemically free" is hereinafter alternatively referred to as "uncomplexed"). More preferably, the vitamin B<sub>3</sub> compound is essentially uncomplexed. Therefore, if the composition contains the vitamin B<sub>3</sub> compound in a salt or otherwise complexed form, such complex is preferably substantially reversible, more preferably essentially reversible, upon delivery of the composition to the skin. For example, such complex should be substantially reversible at a pH of from about 5.0 to about 6.0. Such reversibility can be readily determined by one having ordinary skill in the art.

More preferably the vitamin B<sub>3</sub> compound is substantially uncomplexed in the composition prior to delivery to the skin. Exemplary approaches to minimizing or preventing the formation of undesirable complexes include omission of materials which form substantially irreversible or other complexes with the vitamin B<sub>3</sub> compound, pH adjustment, ionic strength adjustment, the use of surfactants, and formulating wherein the vitamin B<sub>3</sub> compound and materials which complex therewith are in different phases. Such approaches are well within the level of ordinary skill in the art.

Thus, in a preferred embodiment, the vitamin B<sub>3</sub> compound contains a limited amount of the salt form and is more preferably substantially free of salts of a vitamin B<sub>3</sub> compound. Preferably the vitamin B<sub>3</sub> compound contains less than about 50% of such salt, and is more preferably essentially free of the salt form. The vitamin B<sub>3</sub> compound in the compositions hereof having a pH of from about 4 to about 7 typically contain less than about 50% of the salt form.

The vitamin B<sub>3</sub> compound may be included as the substantially pure material, or as an extract obtained by suitable physical and/or chemical isolation from natural (e.g., plant) sources. The vitamin B<sub>3</sub> compound is preferably substantially pure, more preferably essentially pure.

### Retinoids

In a preferred embodiment, the compositions of the present invention also contain a retinoid. The vitamin B<sub>3</sub> compound and retinoid provide unexpected benefits in regulating skin condition, especially in therapeutically regulating signs of skin aging, more especially wrinkles, lines, and pores. Without intending to be bound or otherwise limited by theory, it is believed that the vitamin B<sub>3</sub> compound increases the conversion of certain retinoids to trans-retinoic acid, which is believed to be the biologically active form of the retinoid, to provide synergistic regulation of skin condition (namely, increased conversion for retinol, retinol esters, and retinal). In addition, the vitamin B<sub>3</sub> compound unexpectedly mitigates redness, inflammation, dermatitis and the like which may otherwise be associated with topical application of retinoid (often referred to, and hereinafter alternatively referred to as "retinoid dermatitis"). Furthermore, the combined vitamin B<sub>3</sub> compound and retinoid tend to increase the amount and activity of thioredoxin, which tends to increase collagen expression levels via the protein AP-1. Therefore, the present invention enables reduced active levels, and therefore reduced potential for retinoid dermatitis, while retaining significant positive skin conditioning benefits. In addition, higher levels of retinoid may still be used to obtain greater skin conditioning efficacy, without undesirable retinoid dermatitis occurring.

As used herein, "retinoid" includes all natural and/or synthetic analogs of Vitamin A or retinol-like compounds which possess the biological activity of Vitamin A in the skin as well as the geometric isomers and stereoisomers of these compounds. The retinoid is preferably retinol, retinol esters (e.g., C<sub>2</sub> - C<sub>22</sub> alkyl esters of retinol, including retinyl palmitate, retinyl acetate, retinyl propionate), retinal, and/or retinoic acid (including all-trans retinoic acid and/or 13-cis-retinoic acid), more preferably retinoids other than retinoic acid. These compounds are well known in the art and are commercially available from a number of sources, e.g., Sigma Chemical Company (St. Louis, MO), and Boehringer Mannheim (Indianapolis, IN). Other retinoids which are useful herein are described in U.S. Patent Nos. 4,677,120, issued Jun. 30, 1987 to Parish et al.; 4,885,311, issued Dec. 5, 1989 to Parish et al.; 5,049,584, issued Sep. 17, 1991 to Purcell et al.; 5,124,356, issued Jun. 23, 1992 to Purcell et al.; and Reissue 34,075, issued Sep. 22, 1992 to Purcell et al.. Other suitable retinoids are tocopheryl-retinoate [tocopherol ester of retinoic acid (trans- or cis-), adapalene {6-[3-(1-adamantyl)-4-methoxyphenyl]-2-naphthoic acid}, and tazarotene (ethyl 6-[2-(4,4-dimethylthiochroman-6-yl)-ethynyl]nicotinate). One or more retinoids may be used herein. Preferred retinoids are retinol, retinyl palmitate,

retinyl acetate, retinyl propionate, retinal and combinations thereof. More preferred are retinol and retinyl palmitate.

The retinoid may be included as the substantially pure material, or as an extract obtained by suitable physical and/or chemical isolation from natural (e.g., plant) sources. The retinoid is preferably substantially pure, more preferably essentially pure.

The compositions of this invention may contain a safe and effective amount of the retinoid, such that the resultant composition is safe and effective for regulating skin condition, preferably for regulating visible and/or tactile discontinuities in skin, more preferably for regulating signs of skin aging, even more preferably for regulating visible and/or tactile discontinuities in skin texture associated with skin aging. The compositions preferably contain from or about 0.005% to or about 2%, more preferably 0.01% to or about 2%, retinoid. Retinol is most preferably used in an amount of from or about 0.01% to or about 0.15%; retinol esters are most preferably used in an amount of from or about 0.01% to or about 2% (e.g., about 1%); retinoic acids are most preferably used in an amount of from or about 0.01% to or about 0.25%; tocopheryl-retinoate [tocopherol ester of retinoic acid (trans- or cis), adapalene {6-[3-(1-adamantyl)-4-methoxyphenyl]-2-naphthoic acid}, and tazarotene are most preferably used in an amount of from or about 0.01% to or about 2%. When the composition contains a retinoid, the vitamin B<sub>3</sub> compound is preferably used in an amount of from or about 0.1% to or about 10%, more preferably from or about 2% to or about 5%.

The pH of the compositions is preferably from about 4 to about 9, more preferably from about 6 to about 8.0.

The balance of the composition is water or an aqueous carrier suitable for topical application to the skin. The water content of the compositions herein is generally from about 30% to about 98.89%, preferably from about 50% to about 95% and especially from about 60% to about 90% by weight.

The compositions of the invention are preferably in the form of a moisturising cream or lotion, which can be applied to the skin as a leave-on product.

The invention is illustrated by the following examples

Examples 1-3

Oil-in-water emulsions are prepared from the following ingredients using conventional formulating techniques.

	Ex 1	Ex 2	Ex 3
Cetyl Alcohol	0.72	0.72	0.72
Stearyl Alcohol	0.48	0.48	0.48
Stearic Acid	0.1	0.1	0.1
PEG-100 Stearate	0.1	0.1	0.1
Arlatone 2121	1	1	1
Methyl Isostearate	1.33	0	0
Isopropyl Isostearate	0	1.33	1.33
Silicone Q21403	2	2	2
Fatty acid ester of sugar <sup>1</sup>	0.67	0.67	0.67
Glycerin	7	7	7
Urea	2	0	0
Carbopol 954	0.68	0.5	0.5
Carbopol 1382	0.1	0.1	0.1
TiO <sub>2</sub>	0.75	0.75	0.75
D-Panthenol	0	0	0.5
Tocopherol Acetate	0	0	0.5
Niacinamide	2	2	2
Retinol	0	0	0.04
BHT	0	0	0.05
Glydant Plus	0.1	0.1	0.1
EDTA	0.1	0.1	0.1
distilled water	qs 100	qs 100	qs 100

<sup>1</sup> A C1-C30 monoester or polyester of sugars and one or more carboxylic acid moieties as described herein, preferably a sucrose polyester in which the degree of esterification is 7-8, and in which the fatty acid moieties are C18 mono- and/or di-unsaturated and behenic, in a molar ratio of unsaturates:behenic of 1:7 to 3:5, more preferably the octaester of sucrose in which there are about 7 behenic fatty acid moieties and about 1 oleic acid moiety in the molecule, e.g., sucrose ester of cottonseed oil fatty acids, e.g., SEFA Cottonate.

Examples IV to VIII

Ingredient	% w/w	%w/w	% w/w	% w/w	% w/w
Deionised Water	to 100	to 100	to 100	to 100	to 100
Glycerine	9.00	5.00	8.00	6.50	7.50
Urea	1.40	1.80	2.20	1.98	1.60
Kronos (TiO <sub>2</sub> ) <sup>1</sup>	0.15	0.15	0.15	0.15	0.15
Arlatone 2121 <sup>2</sup>	0.0	0.50	1.50	0.60	0.50
Carbopol 1382 <sup>3</sup>	0.05	0.20	0.08	0.12	0.05
Carbopol 954 <sup>4</sup>	0.70	0.63	0.68	0.60	0.70
Sodium Hydroxide (40% Soln)	0.80	1.00	0.80	0.85	0.75
Hydrofol Acid	0.08	0.09	0.10	0.12	0.13
Myrj 59 <sup>5</sup>	0.09	0.10	0.09	0.12	0.10
Stearyl Alcohol	0.50	0.38	0.40	0.32	0.48
Cetyl Alcohol	1.20	0.85	1.00	0.72	0.72
Propyl Paraben	0.29	0.25	0.15	0.15	0.18
Finsolv TN <sup>6</sup>	0.00	1.2	0.00	0.5	0.5
SEFA Cottonate <sup>7</sup>	0.2	1.50	1.50	0.75	1.80
Methyl Isostearate	1.33	0.2	0.75	1.5	0.00
Methyl Paraben	0.20	0.20	0.20	0.20	0.20
Phenoxytol	0.40	0.40	0.40	0.40	0.40
EDTA	0.10	0.10	0.10	0.10	0.10
DC Q2-1403 <sup>8</sup>	2.00	1.60	1.60	1.80	1.50
NaCl	0.02	0.02	0.02	0.02	0.02
<b>Total</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>

1. Supplied by Kronos, 4 Place Ville Marie # 500, Montreal, Quebec, Canada
2. Supplied by ICI Surfactants, PO Box 90, Wilton Centre, Middlesborough, Cleveland, TS6 8JE
3. B.F. Goodrich, 9911 Brecksville Road, Brecksville, OH 44141, USA
4. B.F. Goodrich, 9911 Brecksville Road, Brecksville, OH 44141, USA
5. PEG 100 Stearate supplied by ICI, PO Box 90, Wilton Centre, Middlesborough, Cleveland, TS6 8JE
6. C12-C15 Alkyl Benzoate Ester supplied by Finetex Inc., PO Box 216, Elmwood Park, New Jersey 07407, USA
7. Supplied by Procter & Gamble, Winton Hill Technical Centre, Cincinnati, OH, USA
8. Supplied by Dow Corning, Kings Court, 185 Kinds Rd, Reading, Berks, RG1 4EX

The compositions IV to VIII are made as follows:

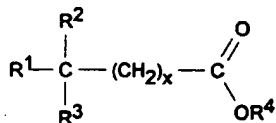
A first premix of thickening agents, methyl paraben, glycerine/TiO<sub>2</sub> premix, Arlatone 2121 when present, and other water soluble ingredients apart from urea, is prepared by admixing in water and heating to about 80°C. A second premix of the oil phase ingredients including the emulsifiers, oil-soluble preservatives, other than silicone gum is prepared by mixing and heating and is added to the aqueous premix.

The resulting mixture is cooled to about 60°C. The NaOH solution, EDTA, silicone gum, and then urea solution (1g dissolved in 1ml of water) are then added to the resulting oil-in-water emulsion and the mixture is cooled before adding minor ingredients. The composition is ready for packaging.

The compositions display improved skin feel, skin smoothness, skin softness and skin care characteristics together with reduced greasiness and excellent rub-in and fast absorption characteristics.

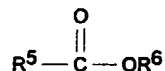
WHAT IS CLAIMED IS:

1. A cosmetic composition suitable for topical application to the skin or hair comprising:
  - (a) a liquid, polyol carboxylic acid ester having a polyol moiety and at least 4 carboxylic acid moieties, wherein the polyol moiety is selected from sugars and sugar alcohols containing from about 4 to about 8 hydroxyl groups, and wherein each carboxylic acid moiety has from about 8 to about 22 carbon atoms, and wherein said liquid polyol carboxylic acid ester has a complete melting point of less than about 30°C;
  - (b) an emollient material selected from compounds having the formula (I):



wherein R<sup>1</sup> is selected from H or CH<sub>3</sub>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently selected from C<sub>1</sub>-C<sub>20</sub> straight chain or branched chain alkyl, and x is an integer of from 1-20,

and compounds having the formula (II):

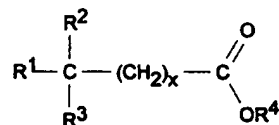


wherein R<sup>5</sup> is selected from optionally hydroxy or C<sub>1</sub>-C<sub>4</sub> alkyl substituted benzyl and R<sub>6</sub> is selected from C<sub>1</sub>-C<sub>20</sub> branched or straight chain alkyl; and mixtures thereof.

2. A composition according to Claim 1 wherein R<sub>1</sub> is H, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, are independently selected from C<sub>1</sub>-C<sub>4</sub> straight chain alkyl and x is 10 to 18, and wherein R<sub>5</sub> is unsubstituted benzyl and R<sub>6</sub> is C<sub>12</sub>-C<sub>15</sub> alkyl.
3. A composition according to Claim 1 or 2 wherein emollient is selected from methyl isostearate, C<sub>12</sub>-C<sub>15</sub> alkyl benzoate ester and mixtures thereof.

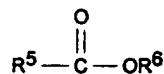
4. A composition according to any of Claims 1 to 3 wherein said liquid polyol carboxylic acid ester contains no more than about 2 free hydroxyl groups.
5. A composition according to any of Claims 1 to 4 wherein said carboxylic acid moieties contain from about 14 to about 18 carbon atoms.
6. A composition according to any of Claims 1 to 5 wherein said polyol moiety is selected from erythritol, xylitol, sorbitol, glucose, sucrose, and mixtures thereof.
7. A composition according to any of Claims 1 to 6 wherein wherein said polyol moiety is sucrose.
8. A composition according to any of Claims 1 to 7 wherein said liquid polyol carboxylic acid ester has a complete melting point below about 27.5°C.
9. A composition according to any of Claims 1 to 8 wherein said liquid polyol carboxylic acid polyester has a complete melting point below about 25°C.
10. A composition according to any of Claims 1 to 9 wherein said liquid carboxylic acid polyol ester is selected from sucrose pentaoleate, sucrose hexaoleate, sucrose heptaoleate, sucrose octaoleate, and mixtures thereof.
11. A composition according to any of Claims 1 to 10 comprising from about 0.1% to about 15%, preferably from about 0.1% to about 10%, more preferably from about 0.1% to about 5% by weight of the emollient material.
12. A composition according to any of Claims 1 to 11 comprising from about 0.1% to about 15%, preferably from about 0.1% to about 10%, more preferably from about 0.1% to about 5% by weight of the liquid, polyol carboxylic acid ester.
13. A composition according to any of Claims 1 to 12 wherein the weight ratio of said liquid carboxylic acid polyol ester to the emollient material is in the range from about 5:1 to 1:5, preferably from about 2:1 to about 1:2.

14. A composition according to any of Claims 1 to 13 wherein the composition is in the form of an emulsion, preferably an oil-in-water emulsion.
15. A composition according to Claim 14 additionally comprising a silicone-containing phase.
16. A composition according to Claim 15 wherein the silicone-containing phase comprises a silicone or mixture of silicones in a level of from 0.1% to 20% by weight, preferably from about 0.1% to about 15%, more preferably from 0.1% to about 10% by weight of composition, and wherein the silicone or silicone mixture comprises a silicone gum having a molecular weight of from about 200,000 to about 4,000,000.
17. A composition comprising:
  - (a) a liquid, polyol carboxylic acid ester having a polyol moiety and at least 4 carboxylic acid moieties, wherein the polyol moiety is selected from sugars and sugar alcohols containing from about 4 to about 8 hydroxyl groups, and wherein each carboxylic acid moiety has from about 8 to about 22 carbon atoms, and wherein said liquid polyol carboxylic acid ester has a complete melting point of less than about 30°C;
  - (b) an emollient material selected from compounds having the formula (I):



wherein R<sup>1</sup> is selected from H or CH<sub>3</sub>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently selected from C<sub>1</sub>-C<sub>20</sub> straight chain or branched chain alkyl, and x is an integer of from 1-20,

and compounds having the formula (II):



wherein  $R^5$  is selected from optionally hydroxy or  $C_1$ - $C_4$  alkyl substituted benzyl and  $R_6$  is selected from  $C_1$ - $C_{20}$  branched or straight chain alkyl; and mixtures thereof.

18. Cosmetic method of treatment of the skin comprising applying to the skin a composition according to any of Claims 1 to 17.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/20566

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) : A61K 7/48 US CL : 424/401; 514/844, 936 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 424/401; 514/844, 936  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) GPI WEBSITE		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,534,265(FOWLER ET AL) 09 July 1996 , col.16 , lines 30-50 , col.17, lines 55-67, col.18, lines 1-15 , col.19, lines 45-60	1-3,17-18
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* *A* *E* *L* *O* *P*	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* *X* *Y* *&*
Date of the actual completion of the international search 14 JANUARY 1998		Date of mailing of the international search report 10 FEB 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer JYOTHSNA VENKAT Telephone No. (703) 308-2351

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/20566

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-16  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims: it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.